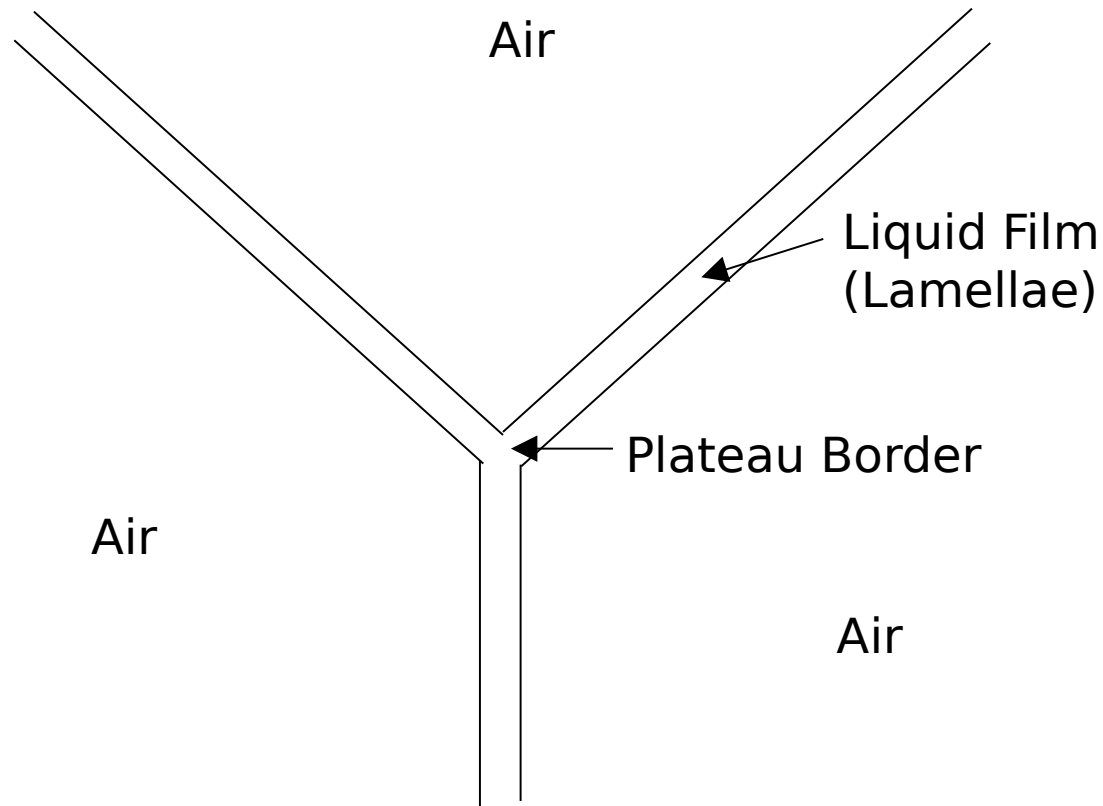# SAS4323 Surfactant

Lecture 6
Foaming

What is a Foam?

- Foam is produced when air or gas is introduced beneath the surface of a liquid that expands to enclose the gas with a film of liquid
  - Collection of bubbles
  - Air inside a liquid film

- Requires
  - Air
  - Liquid
  - Surfactant

2

Structure of Foam

Air

Liquid Film
(Lamellae)

Plateau Border

Air

Air

Intersection Point of Three Bubbles

Structure of Foam

- Honeycomb structure with two-sided thin films called "lamellae"

- when 3 or more bubble meet, a 'Plateau border' or "Gibbs triangles" is formed

- The curvature in the lamellae is greatest in the plateau borders

Foam Destruction

- Foams are destroyed when liquid drains out from between the two parallel surfaces of the lamella

- When the film reaches a critical thickness (50-100Å), it collapses

- Å = 10^{-10}m

Drainage inside Foam

- Drainage is caused by
  - Hydrostatic Pressure
    - Liquid flow under gravity
    - Lamellae are thinnest in upper region and thickest in the lower region
  - Pressure from Curvature
    - Lamellae as parts of bubbles, have different pressure at different curvature (Young-Laplace Equation)

Gravity Drainage of Foam

Thinning of Film

Gravity Flow
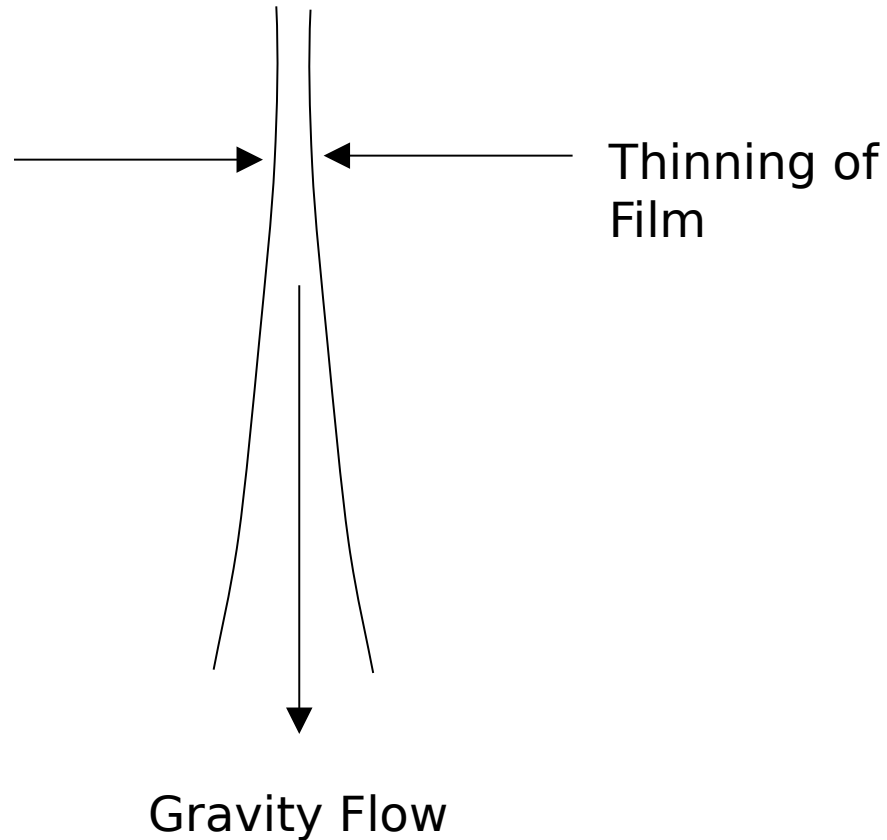
Types of Foams

- Persistent foam (or metastable foams)
  - Lifetime = hours or days

- Transient foam (or unstable foams)
  - Lifetime = less than a minute

Film Elasticity

- For a liquid to foam (persistently or transiently), the liquid membrane surrounding the bubbles must possess a special form of elasticity
  - Any applied stresses that tend toward local thinning or stretching of the membrane are rapidly opposed and counterbalanced by restoring forces, like the stretching of a rubber band

Film Elasticity

- A necessary condition for the production of foam but not sufficient for the formation of persistent foam

$$\gamma_2 > \gamma_1$$

$$\gamma_1 \qquad \gamma_1$$

$$\gamma_2$$

$$\gamma_2 - \gamma_1 = \underset{\text{Restoring force}}{\longrightarrow} \qquad \underset{\text{Restoring force}}{\longleftarrow} = \gamma_2 - \gamma_1$$
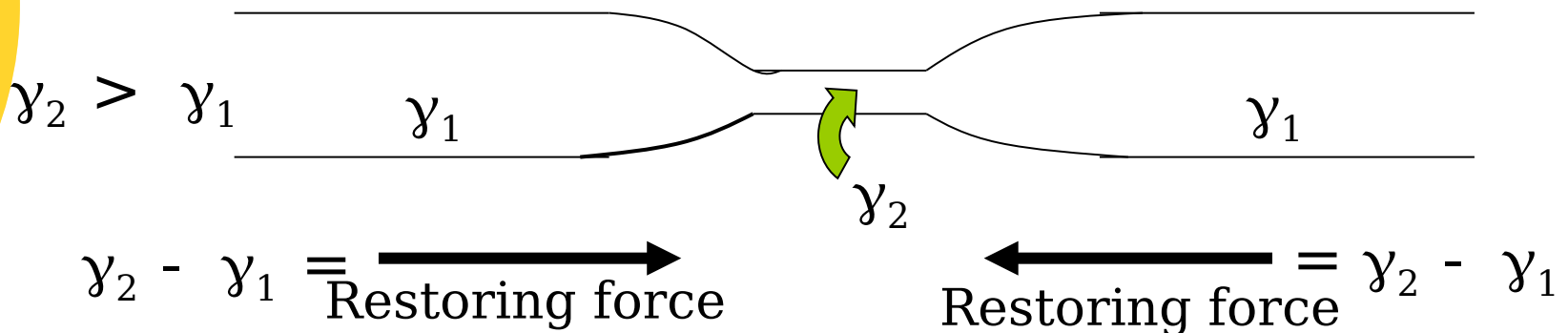
- This film elasticity is only possible if a surfactant is present

Foam Persistence

Factors Affecting Foam Persistence:

- Drainage of liquid inside lamellae

- Electrical double layer effect

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Foam Persistence
Drainage of Liquid

- Mechanism must be present to retard the loss of liquid and gas from the foam and to prevent rupture of the lamellae

- Drainage by gravity
  - important in thick lamellae
  - affected by viscosity
    - Increase viscosity, retarding drainage, more stable foams

Foam Persistence
Drainage of Liquid

- Drainage by pressure due to curvature
  - Important in thin lamellae
  - Depends on the existence of pressure difference at various points in the lamellae
  - Greater the difference between R_B and R_A, greater the curvatures difference, greater the difference in pressure difference causing the drainage
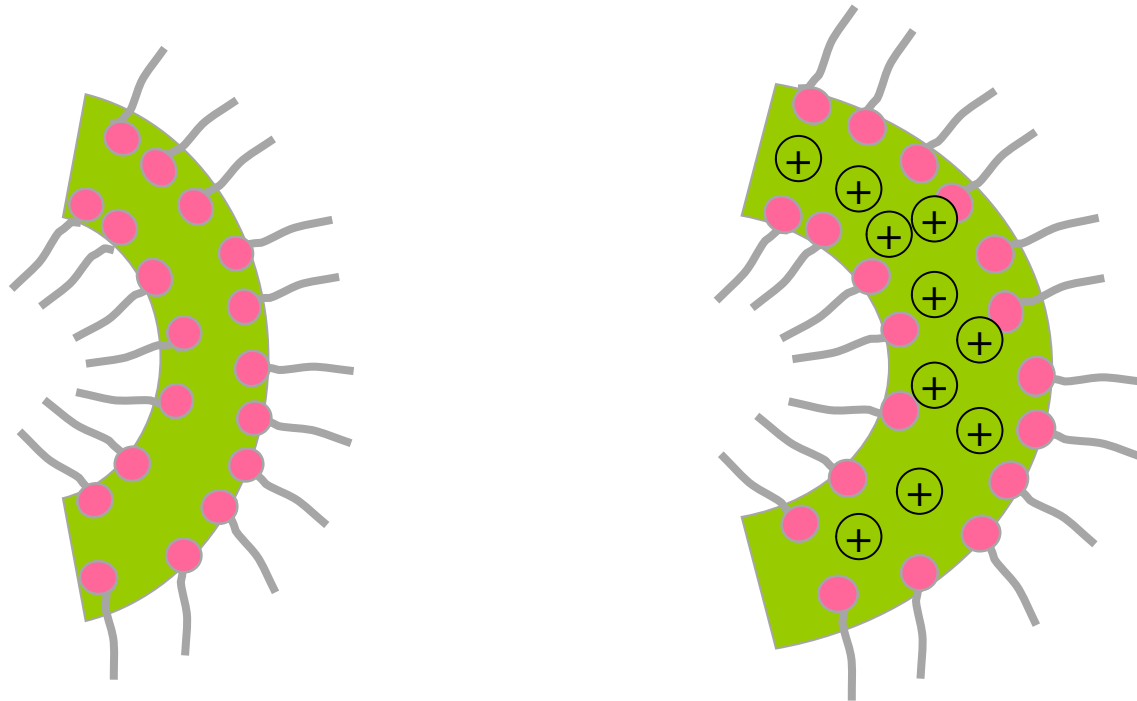
Foam Persistence
Electrical double layer

- Thinning of foam film may be prevented by the existence and thickness of electrical double layer
  - Electrostatic repulsion between the 2 sides of the film.
    - Maintaining Thickness of the Lamella
- High osmotic pressure due to large concentration of counter-ions present

Foam Persistence
Double Layer in Lamellae

Nonionic surfactants

- Nonionic surfactants generally produce less foam and much less stable foam than ionic surfactants in aqueous media

- These are probably due to:
  - Large surface area per molecule
  - Absence of highly charges surface films

Foam Measurements

- Foaming ability of a surfactant depends on:
  - Concentration
  - Temperature
  - Water hardness
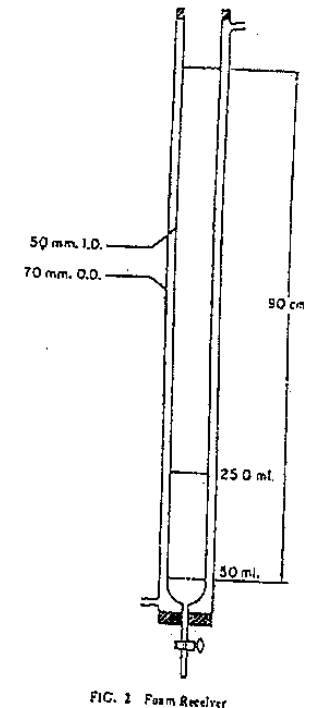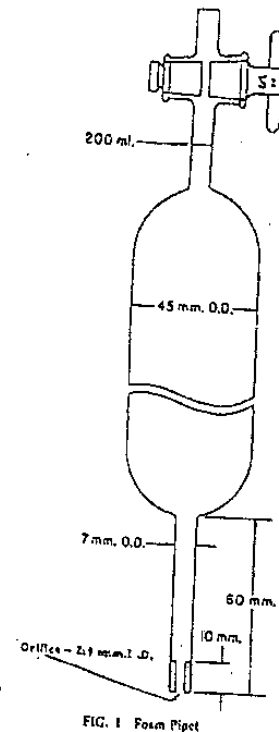 - Method used to produce the foam

Ross-Miles method

- Foam created by impinging(碰撞) a stream of liquid onto a pool of liquid
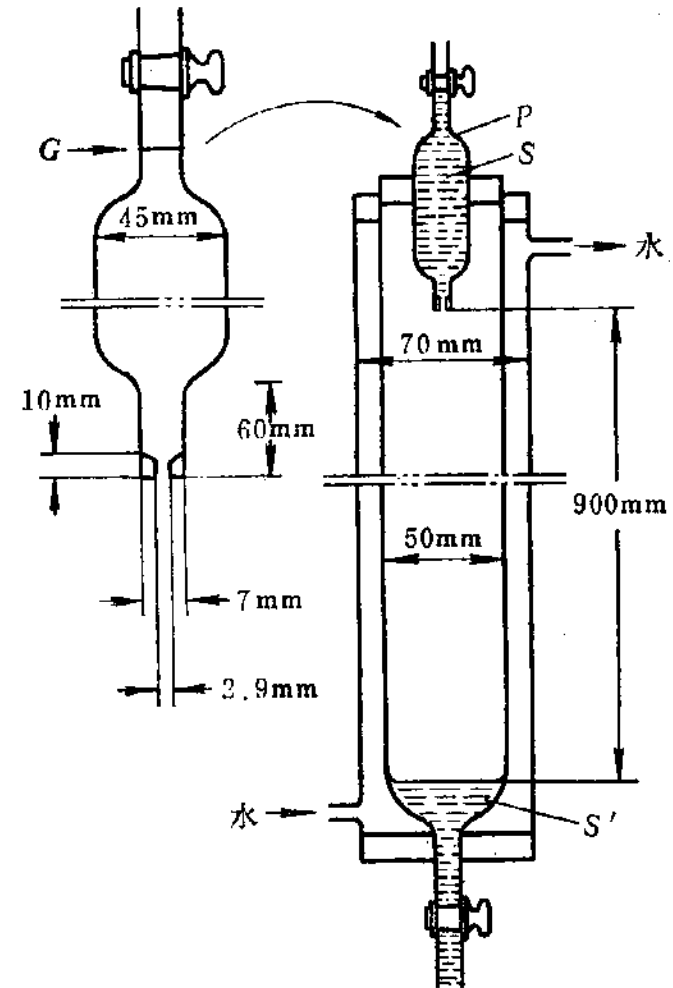
Ross-Miles method

- Two Characteristics are Measured
  - Foam production, measured by height of foam initially produced
  - Foam stability, measured by height of foam after a given amount of time

FIG. 1 Foam Pipet

200 ml.
45 mm. O.D.
7 mm. O.D.
60 mm.
10 mm.
Orifice – 2.9 mm. I.D.

FIG. 2 Foam Receiver

50 mm. I.D.
70 mm. O.D.
90 cm
25 0 ml.
50 ml.

Surfactants concentrations required to attain maximum foam height, MFH(Ross-Miles Method, 60°C)

Surfactant	cmc (mM)	Concentration for MFH (mM)
$C_{12}H_{25}SO_3^-Na^+$	11	13
$C_{12}H_{25}SO_4^-Na^+$	9	5
$C_{14}H_{29}SO_3^-K^+$	3	3
$C_{14}H_{29}SO_4^-Na^+$	2.3	3
$C_{16}H_{33}SO_3^-K^+$	0.9	0.8
$C_{16}H_{33}SO_4^-Na^+$	0.7	0.8
$p\text{-}C_8H_{17}C_6H_4SO_3^-Na^+$	16	13
$p\text{-}C_{10}H_{21}C_6H_4SO_3^-Na^+$	3	4.5
$p\text{-}C_{12}H_{25}C_6H_4SO_3^-Na^+$	1.2	4
$o\text{-}C_{12}H_{25}C_6H_4SO_3^-Na^+$	3	4
$(C_8H_{17})_2CHSO_4^-Na^+$	2.3	4

Foaming Agent

Efficiency(效率)

- Bulk phase concentration required to produce a significant amount of foam
- Often measured by CMC, i.e. the lower CMC the more efficient the surfactant as a foaming agent

Foaming Agent

Effectiveness(效果)

- Maximum foam height obtained regardless of concentration

- depends on:
  - Its effectiveness in reducing the surface tension of the foaming solution
  - The magnitude of its intermolecular cohesion forces

Emulsion

Definition of an Emulsion

- '*Significantly Stabilized*' suspension of particles of liquid droplets of a certain size within a second immiscible liquid

- Thermodynamically Unstable
  - Eventually revert to a two-phase system

Classification of Emulsion

- Classification based on size of dispersed particles
  - Macro-emulsion – 0.2 to 50 μm
    - Opaque(不透明)
    - Visible under microscope
  - Mini-emulsion – 0.1 to 0.4 μm
  - Micro-emulsion – 0.01 to 0.2 μm (10 – 200nm)
   - Transparent or semi-transparent

Light Dispersion of Colloid/Emulsion

Diameter of Dispersed Particles	Appearance
> 1 μm	Milky White
0.1 – 1 μm	Bluish White
0.05 – 0.1 μm	Gray, Semi-transparent
< 0.05 μm	Transparent

Classification of Emulsion

- Classification based on dispersed phase:
  - Oil-in-water (O/W) emulsion
    - Dispersion of oil droplets in water
    - Continuous phase – Water
    - Dispersed phase - Oil
  - Water-in-Oil (W/O) emulsion
    - Dispersion of water droplets in oil
    - Continuous phase – Oil
    - Dispersed phase - Water

Oil – in – Water Emulsion
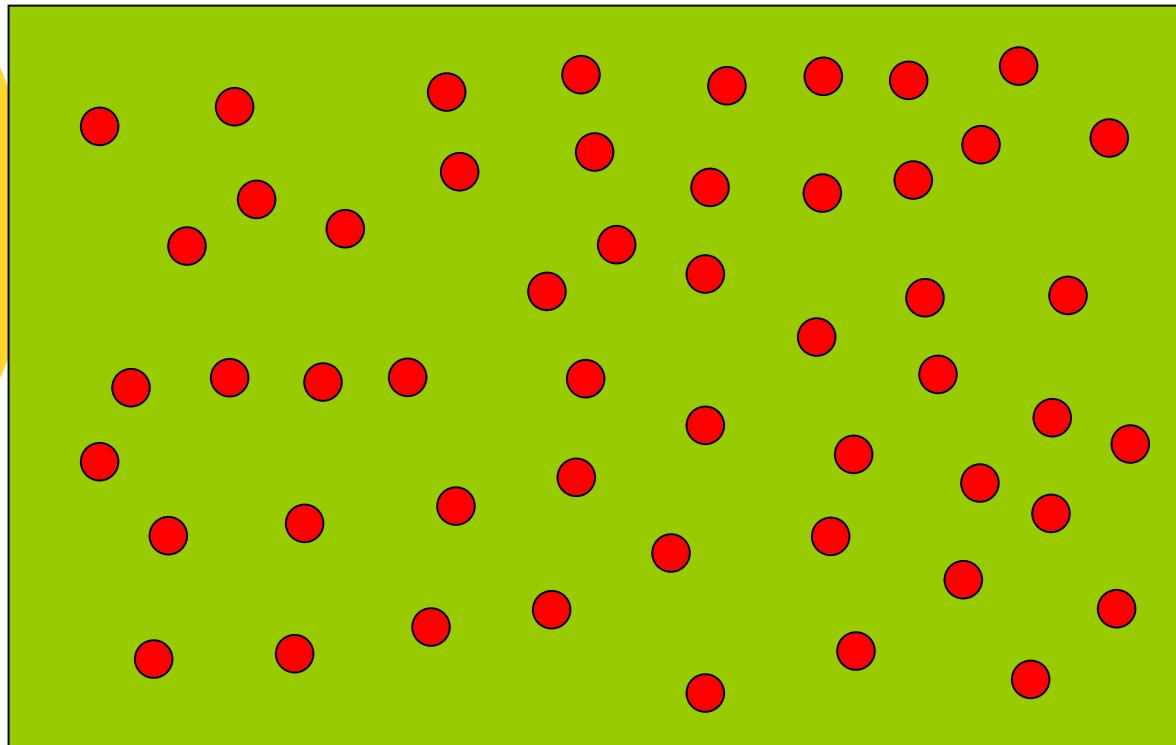
● Oil Droplet

Water

Comparison O/W and W/O Emulsion

Oil in Water Emulsion	Water in Oil Emulsion
Dilute by Water	Dilute with Oil
Good Conductance	Bad Conductance
Color by Water Soluble Dye	Color by Oil Soluble Dye

Emulsification

- Formation of emulsion from two immiscible liquid
- A third component (components) called "emulsifying agent" (usually a surface-active agent) must be present to stabilize the system

Functions of Emulsifying Agent

- Instability is the result of increase in surface area due to formation of dispersed phase which increases the system free energy
- Reduce thermodynamic instability
  - Reduced interfacial tension between liquids
- Decrease rate of coalescence(聚结) of the dispersed liquid particles by formation barriers between them
  - Mechanical
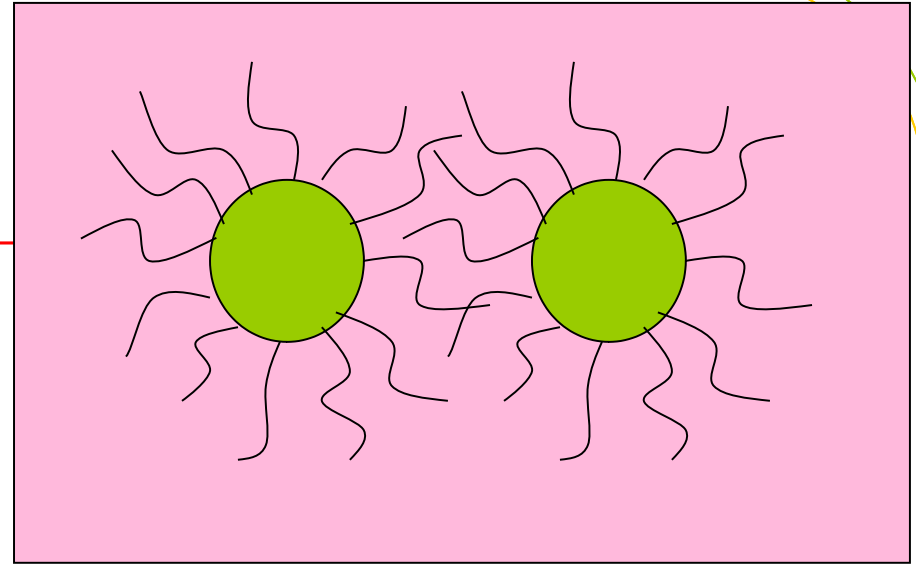 - Steric

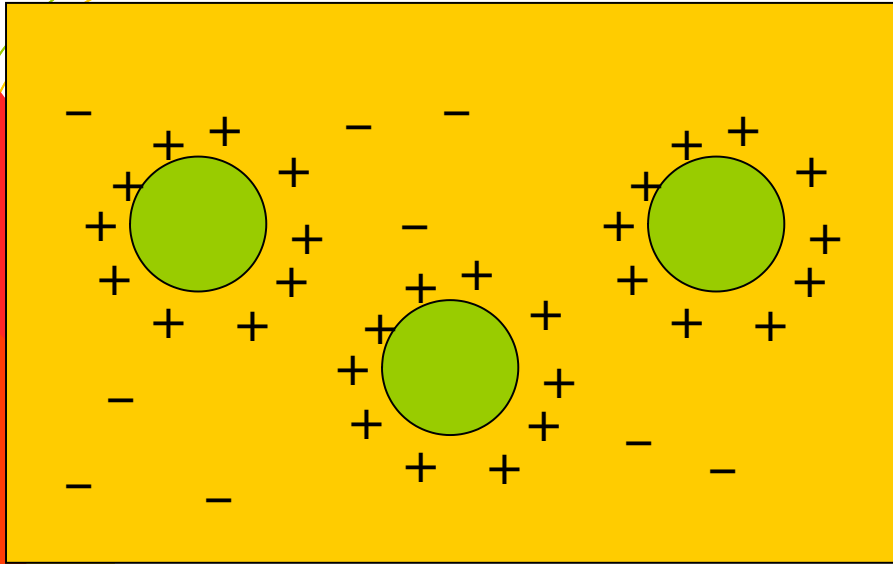# Factors Affecting Formation of Emulsion

- Type of emulsion formed by "water" and "oil" depends on :
  - Nature of emulsifying agent
  - Process used in preparing the emulsion
  - Relative proportions of 'oil' and 'water' present

Bancroft Rule

- o/w emulsions are generally produced by emulsifying agents that are more soluble in 'water' than in 'oil' phase
- The reverse is true for w/o emulsions

Factors Affecting Emulsion Stability

- Stability = resistance to coalescence

  - Measured by rate of coalescence
- Physical nature of interfacial film
  - Strong lateral intermolecular forces between surfactant to hold together
  - High film elasticity
    - Mixture of two or more surfactants
- Existence of electrical or steric barrier on the droplets

Colloidal particles in solution stabilized by:
1. electrostatic repulsion due to surface charges (left) or
2. by steric repulsion of grafted long-chain, polymeric molecules (right)

Factors Affecting Emulsion Stability

- Viscosity of the continuous phase
- The motion of droplets is characterized by the diffusion coefficient

$$D = \frac{kT}{6\pi r\eta}$$

- Where r is the radius, η is the viscosity of outer phase
- as D is reduced, rate of coalescence are reduced and more stable for the emulsion

Factors Affecting Emulsion Stability

- Size distribution of droplets
  - the larger the size of droplets, less interfacial surface per unit volume, the more thermodynamically stable
  - Emulsion with uniform size distribution is more stable
- Phase volume ratio
  - the instability of the system increase as the volume of the dispersed phase increases

Factors Affecting Emulsion Stability

- Temperature
  - Interfacial tension
  - Interfacial film
  - Relative solubility of emulsifying agent in two phases
  - Vapor pressure and viscosity of liquids
  - Thermal agitation of dispersed particles

Selecting Emulsifying Agents

- The HLB method (Hydrophile - Lipophile Balance Method)
- A number between 0 and 20 can be assigned to an emulsifying agent
- It can be based on experimental emulsification data
- Or

Selecting Emulsifying Agents

- HLB number can be calculated from the structure of the emulsifying agent by

$$HLB = 20 \times \left[\frac{M_H}{M_H + M_L} \right]$$

Where M_H = Formula Weight of Hydrophilic Portion

Where M_L = Formula Weight of Lipophilic Portion

- Usually HLB < 10 lipophilic, HLB > 10 hydrophilic

Selecting Emulsifying Agents

- A similar range of numbers can be assigned to various substances that are frequently emulsified, e.g. oil, lanolin, paraffin wax, xylene, etc.
  - Note: value may depend on which phase it is in

Selecting Emulsifying Agents

- An emulsifying agent (or a combination of emulsifying agents) is selected whose HLB number is about the same as that of the ingredients to be emulsified
  - Note: weighted average of assigned numbers is always used for mixtures

Example:

For a mixture of 20% paraffin wax (HLB = 10) and 80% aromatic mineral oil (HLB = 13)

HLB number = (10 x 0.20) + (13 x 0.80)
= 12.4

To emulsify this mixture, a mixture of 60% surfactant with HLB = 16.9 and 40% surfactant with HLB = 5.3 could be tried.

HLB = (16.9 x 0.06) + (5.3 x 0.40)
= 12.2

- Materials with high HLB values are o/w emulsifiers, with low HLB values are, w/o emulsifiers.
  - HLB value of 3-6 is recommended range for w/o emulsification

HLB	Application
1 – 3	anti-foaming agent
3 – 6	w/o emulsifying agents
7 – 9	wetting agents
8 – 18	o/w emulsifying agents
13 – 15	detergents
15 - 18	solubilizing agents

- Water solubility of the surfactant can be used as a rough guideline for its HLB value:

Behavior in water	HLB Range
No dispersibility	1-4
Poor dispersion	3-6
Milky dispersion after vigorous agitation	6-8
Stable milky dispersion (upper end almost translucent)	8-10
Form translucent to clear	10-13
Clear solution	13+

Surfactant	Commercial Name	HLB
Sorbitan trioleate	SPAN 85	1.8
Sorbitan tristearate	SPAN 65	2.1
Propylene glycol monostearate	"PURE"	3.4
Glycerol monostearate	ATMUL 67	3.8
Sorbitan monooleate	SPAN 80	4.3
Sorbitan monostearate	SPAN 60	4.7
Diethylene glycol monolaurate	GLAURIN	6.1
Sorbitan monolaurate	SPAN 20	8.6
Glycerol monostearate	ALDO 28	11
Polyoxyethylene(2) cetyl ether	BRIJ 52	5.3
Polyoxyethylene(10) cetyl ether	BRIJ 56	12.9
Polyoxyethylene(20) cetyl ether	BRIJ 58	15.7
Polyoxyethylene(6) tridecyl ether	RENEX 36	11.4
Polyoxyethylene(12) tridecyl ether	RENEX 30	14.5
Polyoxyethylene(15) tridecyl ether	RENEX 31	15.4

Question 1

- Calculate the percentage composition of surfactant A in a mixture of surfactant A and B if the Hydrophile–Lipophile Balance (HLB) of the mixture is 9.9.

-

- **GIVEN:**
- HLB of surfactant A is 12.3
- HLB of surfactant B is 8.6

Answer

- Let x be the percentage of surfactant A and (1 – x) be the percentage of surfactant B
- $9.9 = x(12.3) + (1 – x)(8.6)$
- $x = 0.3514$

- There are 35.14% of A

Question 2

- Suppose 100g of water and 250g of oil is mixed to form an emulsion. 25% of the molar mass of oil molecule can be considered as polar. What is the HLB number of the oil and the emulsion?

Answer

$$\mathrm{HLB_{oil}} = 20 \text{ X } \frac{250(0.25)}{250} = 5$$

$$\mathrm{HLB_{emulsion}} = \frac{100}{100+250}(20) + \frac{250}{100+250}(5) = 9.29$$